U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-280 784

Verification of a Particle Size Correction Method for X-Ray Fluorescence Spectrometric Analysis of Environmental Samples

Environmental Sciences Research Lab, Research Triangle Park, N C

11 Oct 77

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

PB 280 784

1. REPORT NO. EPA-600/J-78-005	2. JOURNAL ARTICLE
3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE: Verification of a Particle Size Correction Method for X-Ray Fluorescence Spectrometric Analysis of Environmental Samples	5. REPORT DATE
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) J. Wagman, J. Miller, and R. Griffin	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS (Same as Box 12)	10. PROGRAM ELEMENT NO. 1AD 712 BD-05 (FY-77)
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U. S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES
REFERENCE: Anal. Chem., 50(1):37-39, January 1978

16. ABSTRACT

Platinum tetraiodide aerosols generated with a spinning disk from solutions in ethanol were used to test a particle size correction factor recently proposed by Criss for the X-ray fluorescence analysis of filter-deposited particulate samples. A set of standards of well-defined particle sizes in the range of 0.7 to 3.0 μm diameter was prepared by collection of these aerosols on Nuclepore filters. Measured Pt-L_α and I-L_α line sensitivities, plotted as a function of particle size, were in quite good agreement with curves predicted by the Criss equation. Problems and procedures in applying the correction factor to environmental samples are discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air Pollution * Aerosols Particle size * Correction Verifying * X ray fluorescence		13B 07D 14B 20F

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)

EPA-600/J-78-005
JOURNAL ARTICLE

Reprinted from ANALYTICAL CHEMISTRY, Vol. 50, Page 37, January 1978
Copyright 1977 by the American Chemical Society and reprinted by permission of the copyright owner

Verification of a Particle Size Correction Method for X-ray Fluorescence Spectrometric Analysis of Environmental Samples

Jack Wagman,* John L. Miller, and Robert J. Griffin

Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711

Robert B. Kellogg

Northrop Services, Inc., P.O. Box 12313, Research Triangle Park, North Carolina 27709

Platinum tetraiodide aerosols generated with a spinning disk from solutions in ethanol were used to test a particle size correction factor recently proposed by Criss [*Anal. Chem.*, 48, 179 (1976)] for the x-ray fluorescence analysis of filter-deposited particulate samples. A set of standards of well-defined particle sizes in the range of 0.7- to 3.0-μm diameter was prepared by collection of these aerosols on Nuclepore filters. Measured Pt Lα and I Lα line sensitivities, plotted as a function of particle size, were in quite good agreement with curves predicted by the Criss equation. Problems and procedures in applying the correction factor to environmental samples are discussed.

X-ray fluorescence spectrometry is becoming a broadly used procedure for the elemental analysis of filter-deposited airborne and waterborne particulate matter (*1*, *2*). To minimize matrix and substrate effects, samples for analysis are preferably collected as thin particle deposits, i.e., less than 100 $\mu g/cm^2$, on thin, low density, membrane filters. In practice, the intensities (above background) of characteristic fluorescence lines are measured and then related to sensitivities established with standard specimens to determine elemental concentrations.

The task of data interpretation is least troublesome if the deposited particles do not penetrate the filter and do not shadow each other in either the incident or fluorescent beams. For such samples, fluorescent sensitivities need only to be corrected for particle size and composition effects where these are significant. Criss (*3*) has considered this type of sample in detail. Using computer-simulated measurements that included a variety of particle shapes, sizes, orientations, and compositions, he has proposed an empirical correction factor

0003-2700/78/0350-0037$01.00/0 © 1977 American Chemical Society

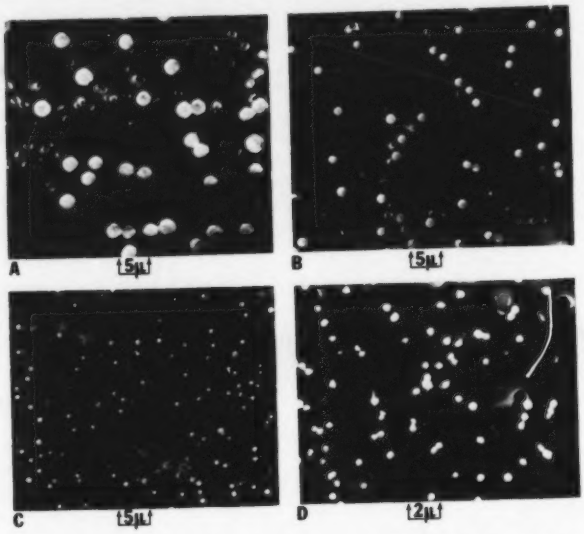

Figure 1. Nuclepore filter deposits of particles generated with a spinning disk from ethanol solutions containing (A) 1000, (B) 200, (C) 40, and (D) 8 mg PtI_4 per 100 mL, respectively

that relates the actual sensitivity, S_i, for element i to the sensitivity, $S_{0,i}$, for infinitesimally-sized particles, by

$$S_i = S_{0,i}/(1 + b_i a_i)^2 \quad (1)$$

where a_i is the particle diameter (in μm) and b_i is an attenuation coefficient that depends on the incident beam spectrum, the fluorescent wavelength, and particle composition. Values of b were calculated (*3*) for 48 elements in over 200 compounds using chromium- or tungsten-target x-ray tubes.

We conducted a laboratory test of Equation 1 using a series of platinum tetraiodide (PtI_4) particle standards of well-defined particle sizes.

EXPERIMENTAL

Particle standards were prepared by depositing spinning-disk-generated aerosols on Nuclepore (Nuclepore Corporation, Pleasanton, Calif.) membrane filters. The selection of PtI_4 as the test material was made because its existence as an amorphous solid facilitated the generation of spherical particles from solution and the greatly divergent b values of its constituent elements (0.023 and 0.14 for the Pt Lα and I Lα lines, respectively, using a Cr-target x-ray tube) provided a reasonably challenging test of Equation 1.

A spinning disk aerosol generator (*4*) was used because of its capability for producing solid particles of fairly uniform and controlled sizes in the range of sizes needed for the test. Solutions of high-purity, research-grade PtI_4 (obtained from Pfaltz & Bauer, Inc.) in anhydrous ethanol were prepared for aerosolization in an ERC Model 8330 (Sierra Instruments, Inc., Carmel Valley, Calif.) generator with a 1-inch diameter stainless steel disk spinning at 60 000 rpm. Since the disk speed was fixed, control of particle size was obtained by varying the PtI_4 concentration. Four solutions with concentrations of 8, 40, 200, and 1000 mg/100 mL were used. Samples of dried aerosols were collected on 47-mm, 0.5-μm pore size, Nuclepore filters that were frame-mounted (*5*) for ease of handling during sampling and subsequent x-ray fluorescence measurement. The sampling pump was protected from contamination by use of a glass fiber filter backup to the Nuclepore filters, and the effluents from both the generator and sampling pump were exhausted to a ventilating hood because of the toxicity of PtI_4.

Fluorescence intensities above background for the Lα lines of platinum and iodine were measured by 20-s counts with the scanning channel of a Siemens MRS-3 simultaneous multi-wavelength spectrometer (*5*) using a Cr-target x-ray tube. The PtI_4 aerosol deposits were also examined in an AMR-900 scanning electron microscope and determinations of particle sizes were made from micrographs.

Table I. Median Particle Sizes of PtI_4 Aerosols Generated by Spinning Disk from Solutions in Ethanol

PtI_4 concn, mg/100 mL	Mass median diameter,[a] μm	Geometric std dev[b]
1000	2.95	1.12
200	1.77	1.14
40	1.05	1.18
8	0.70	1.19

[a] The mass median or 50th percentile diameter (D_{50}) defines the particle size that divides the total mass such that half is accounted for in smaller particles (and half in larger particles). [b] The geometric standard deviation (σ_g) is the standard deviation of the particle size frequency mass distribution expressed as a ratio. For a monodisperse sample σ_g is unity. For a log normal distribution, which these particle samples approximated, σ_g is calculated from either D_{84}/D_{50} or D_{50}/D_{16}, where D_{84}, D_{50}, and D_{16} are the 84th, 50th, and 16th percentile diameters, respectively, in cumulative plots of particle size against percent of total mass in particles smaller than a given size.

Table II. Measurement of Lα Line Sensitivities for Pt and I in PtI_4 Aerosol Deposits Varying in Particle Size

PtI_4 aerosol deposit MMD	Fluorescence intensity, counts/s		Deposit mass,[a] μg/cm^2		Sensitivity, counts/s per μg/cm^2	
	Pt Lα	I Lα	Pt	I	Pt Lα	I Lα
mm						
2.95	2275	8301	38.9	65.3	58.5	127
1.77	736.5	3554	11.0	18.2	67.0	195
1.05	434	2560	6.64	11.7	65.4	219
0.70	162.7	1116	2.74	4.74	59.4	235

[a] By neutron activation analysis.

RESULTS

The set of PtI_4 aerosols generated by spinning disk and deposited on Nuclepore filters is illustrated by the scanning electron micrographs in Figure 1. It can be seen that each of the aerosol deposits consisted of near-spherical, fairly uniform-sized, particles distributed on the filters with little or no stacking. Size measurements were made of about 100 randomly selected particles in each deposit. Table I summarizes the particle size parameters for the aerosols generated from the four solutions of PtI_4 in ethanol.

The samples of deposited PtI_4 aerosols thus included a range of particle sizes (i.e., 0.7 to 3.0 μm mass median diameter) that corresponded to a significant portion of size ranges often encountered in source and ambient aerosols.

Fluorescent intensities above background, I_i, measured for the photon-excited Lα lines of platinum and iodine, respectively, from each of the PtI_4 deposits are listed in Table II. The corresponding sensitivities, S_i, can be calculated from the relation

$$S_i = I_i/M_i \quad (2)$$

if the deposit masses per unit area, M_i, are known. Platinum and iodine deposit concentrations were determined by neutron activation analysis and the results are listed in Table II along with the resultant Pt Lα and I Lα line sensitivities.

The neutron activation analyses for platinum and iodine in the aerosol deposits indicate a deficiency of iodine for PtI_4 stoichiometry. The values found correspond to mixtures containing about 87% PtI_4 and 13% platinum by mass. On the other hand, neutron activation analysis for platinum and

Table III. Measurements of s_0 for Platinum and Iodine Using Vacuum-Evaporated Films

Element	Film		Element concn, $\mu g/cm^2$	Lα line	
	Composition	Thickness, μm		Intensity, counts/s	Sensitivity, counts/s per $\mu g/cm^2$
Pt	Pt	0.013	28	1837	65.6
I	KI	0.008	1.95	559.6	287

iodine in the bulk sample from which the deposits were prepared gave results that were nearly stoichiometric for PtI_4, indicating substantial release of iodine during the steps leading to generation and deposition of the test aerosols.

The Criss particle size correction procedure (Equation 1) predicts the following Pt Lα and I Lα line sensitivities for these aerosol deposits:

$$S_I = \frac{S_{0,I}}{(1 + 0.14\,a)^2} \tag{3}$$

and

$$S_{Pt} = 0.87\,\frac{S_{0,Pt}}{(1 + 0.023a)^2} + 0.13\,\frac{S_{0,Pt}}{(1 + 0.087a)^2} \tag{4}$$

where 0.14 and 0.023 are the values of b calculated by Criss (for a Cr-target tube) for analysis of iodine and platinum, respectively, in PtI_4, and 0.087 is the corresponding b value for analysis of platinum in its uncombined form. Standards consisting of very thin vacuum evaporated films (about 0.01 μm in height) of platinum and KI on Mylar membranes provided a good approximation for the condition of negligible particle size or thickness, and hence were used to obtain values for $S_{0,Pt}$ and $S_{0,I}$ (see Table III).

Figure 2 summarizes the results of this test of the proposed empirical correction procedure. The measured Pt Lα and I Lα line sensitivities for the set of four filter-deposited aerosols are shown plotted as a function of the deposited particle mass median diameters. Equations 3 and 4 are represented by the two curves drawn on the same graph. The quite good agreement seen between the measured platinum and iodine sensitivities and those predicted by Equations 3 and 4 demonstrate the essential validity of Criss' proposed correction factor for particle size and composition. The largest observed discrepancy in the test occurred for the iodine sensitivity in particles of 2.95-μm diameter, where the correction factor, $(1 + ba)^2$, is 2.0; even here the calculated sensitivity was only 13% higher than the measured value. The results overall showed a relative standard deviation of 8%, well within expected errors in measuring elemental concentrations, fluorescence intensities, and particle size.

DISCUSSION

The results of this test with PtI_4 particles provide assurance that the effects of particle size and composition on x-ray fluorescence intensity can be accounted for by the simple empirical correction proposed by Criss. While this should give the analyst a measure of confidence in applying the correction, he still faces some formidable problems in dealing with real samples when large correction factors are involved.

A problem over which the analyst can exercise some control is that of interparticle shielding. Through the selection of a suitable filter substrate and precautions during sample collection, the incidence of particle stacking can be reduced to

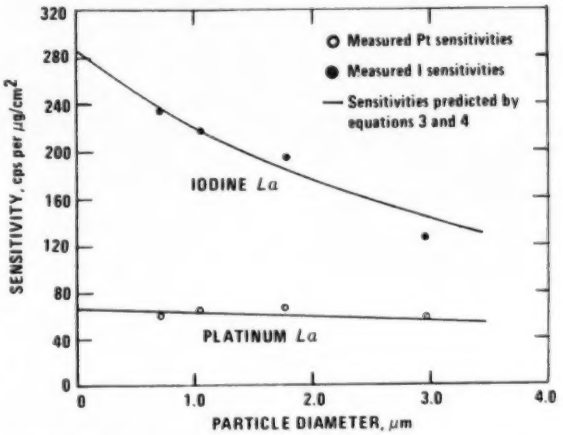

Figure 2. Measured and predicted Pt Lα and I Lα line sensitivities as a function of PtI_4 particle size

negligible proportions. The major problems in applying the correction are those of determining, for each element to be analyzed, appropriate values for the particle size parameter, a, and the particle composition parameter, b, in rather complex samples, e.g., airborne particulate deposits, that are as yet poorly defined. Criss (3) has discussed these uncertainties in some detail, and suggested, as a possible solution, the selection of measurement strategies that minimize the particle effects. Such measures, however, may often be impracticable. An alternative approach that may be feasible for certain types of samples involves the separation, preferably during the sample collection process, of particles into discreet size fractions. The uncertainty in selecting the appropriate particle size parameter is thus greatly reduced. Since compounds are often present in narrow size ranges, this procedure may also help in providing samples for analysis that are more clearly defined in terms of composition.

ACKNOWLEDGMENT

We express appreciation to J. W. Criss, L. S. Birks, and J. V. Gilfrich, of the Naval Research Laboratory, for valuable discussions, and to J. P. F. Lambert for the neutron activation analyses.

LITERATURE CITED

(1) L. S. Birks and J. V. Gilfrich, *Anal. Chem.*, **48**, 273R (1976).
(2) "X-Ray Fluorescence Analysis of Environmental Samples", T. G. Dzubay, Ed., Ann Arbor Science Publishers, Ann Arbor, Mich., 1977.
(3) J. W. Criss, *Anal. Chem.*, **48**, 179 (1976).
(4) K. T. Whitby, D. A. Lundgren, and C. M. Peterson, *Int. J. Air Water Pollut.*, **9**, 263 (1965).
(5) J. Wagman, "Chemical Composition of Atmospheric Aerosol Pollutants by High Resolution X-Ray Fluorescence Spectrometry", in "Colloid and Interface Science", Vol. II: Aerosols, Emulsions, and Surfactants, M. Kerker, Ed., Academic Press, New York, N.Y., 1976.

RECEIVED for review August 18, 1977. Accepted October 11, 1977. Mention of company or product names is not intended as endorsement by the U.S. Environmental Protection Agency.